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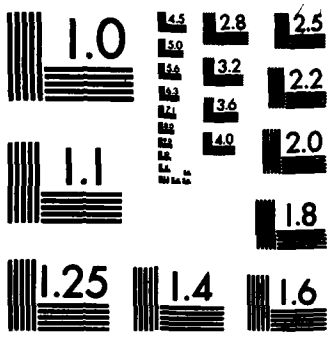

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TECHNICAL REPORT 8301

IDENTIFICATION OF XENOBIOTIC CONTAMINANT OF FIELD WATER SUPPLY SYSTEM DESIGNED FOR RAPID DEPLOYMENT FORCE

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FEBRUARY 1983

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Analysis of methylene chloride extract of water from a field storage and distribution system tested at Fort Irwin, CA, in September 1982, was performed at US Army Medical Bioengineering Research and Development Laboratory November 22-24, 1982, and the previously unidentified major organic contaminant was shown to be 5,8,11,13,16,19-hexaoxatricosane (common names: butylcarbitol formal and Cryoflex).

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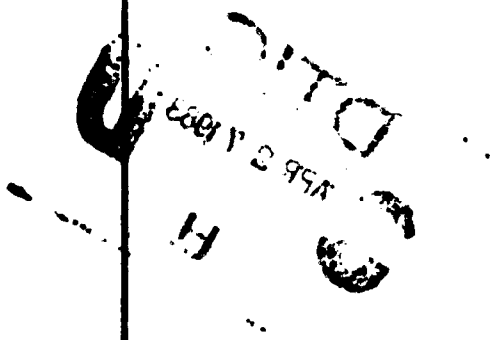

ACKNOWLEDGMENT

We are grateful to Ms. Linda Szafranich of Chemical Systems Laboratory, Aberdeen Proving Ground, MD 21010, for informing us of her NMR analysis, which confirmed our deduction based on the mass spectral and infrared data alone.

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INTRODUCTION

The US Army has developed and/or procured a number of new field equipment items to treat, store, and distribute potable water. During September 1982, the Army Quartermaster School set up and tested the core components of the field water supply system which was designed to support the Rapid Deployment Force. The test was performed under simulated desert combat conditions at Fort Irwin, CA. Major equipment items evaluated were: 150,000 gal/day reverse osmosis water production unit, tactical water storage and distribution system, 4,570 gallon semitrailer-mounted collapsible tank, small water chiller, and forward area water point supply system. A number of ancillary devices were used in support of the major equipment items.

During the field test trials, water samples were taken at points throughout the train of water treatment, storage, and distribution equipment units. The water samples were analyzed for inorganic and organic chemicals and indicator microorganisms of importance for the protection of human health. While most constituents in the potable product waters of the system were identified and were within normal safe drinking water criteria levels, one organic constituent was detected in concentrations exceeding 1,000 times those of the trace organics, and could not be identified by the Army laboratory performing the analyses.

Because of the urgency and importance of demonstrating the viability of the field water equipment, US Army Medical Bioengineering Research and Development Laboratory (USAMBRDL) was verbally requested by the Army Office of The Surgeon General[1] and the Office of the Deputy Chief of Staff for Logistics[2] to provide timely assistance in the identification of the unknown water sample constituent. An extract known to contain the contaminant was provided to USAMBRDL by the Army laboratory responsible for the field test analyses. This report describes the rapid response and the process by which USAMBRDL identified the compound within 3 days of receipt of the extract, and points to the medical implications associated with its ingestion.

OBJECTIVE

The objective of this study was to provide immediate support in the identification of an unknown organic chemical contaminant from potable field waters produced in a test of Army field water treatment, storage, and distribution equipment.

MATERIALS AND METHODS

Mass spectra were determined with a Hewlett Packard 5985B gas chromatograph/mass spectrometer/data system (GC/MS/DS) equipped with a 25 m x 0.2 mm ID fused silica capillary column (cross-linked OV-1, 11 μm thick) interfaced directly to the source. Source temperature was 200°C unless noted otherwise. For CI (chemical ionization) spectra, methane was introduced through a packed column to give a source pressure of 2-3 x 10^{-4} torr, and the

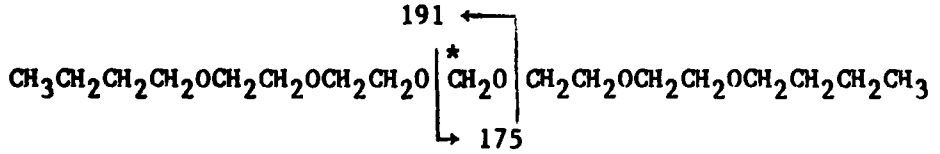
sample was injected into the capillary column (splitless mode). Injection temperature was 250°C, and the GC oven was programmed from 100° to 250°C at 20°C/min with an initial hold of 1 minute.

RESULTS AND DISCUSSION

The sample, received as a methylene chloride solution, was subjected to GC/MS in EI (electron impact) and PCI (positive chemical ionization) mass spectrometry modes. No match for the EI mass spectrum (Fig. 1) was found in the NBS spectral library. The structure was deduced as follows:

Since no unambiguous molecular weight information was found from the CI mass spectrum under normal conditions (Fig. 2), the source temperature was lowered to 100°C to minimize fragmentation. Under these conditions, the base peak was still m/z 175; but, in addition, the typical pattern for a compound of molecular weight M — namely M+1 (m/z 337), M+29 (m/z 365), M+41 (m/z 377) — was observed (Fig. 3).[3] Thus, a molecular weight of 336 was established.

The infrared (IR) spectrum (Fig. 4) showed C-O absorption (1100-1150 cm^{-1}), but no OH, C=O, or C=CH bands were present. The absence of clusters or extra peaks in the mass spectra due to natural abundance isotopes precluded the presence of chlorine, bromine, or sulfur. The presence of nitrogen was considered unlikely because at least two atoms would be necessary (for an even molecular weight), and there was no evidence for the more common N-containing functional groups in the IR spectrum. To calculate molecular formulae for all possible combinations of C, H, and O which give MW 336, a computer program was used. Only the possibilities with 0, 1, and 2 units of unsaturation (double bonds or cycles) were considered: $C_{17}H_{36}O_6$(0), $C_{16}H_{32}O_7$(1) and $C_{15}H_{28}O_8$(2). A survey of recent Chemical Abstracts decennial indices (1957-1976) showed only hydroxyl- and/or carbonyl-containing entries for the latter two formulae, and the only entry for $C_{17}H_{36}O_6$ lacking these functional groups was the compound 5,8,11,13,16,19-hexaoxatricosane. The mass spectral fragmentation pattern, summarized below, is in complete accord with this assignment. The compound, symmetrical about the central acetal carbon (*),



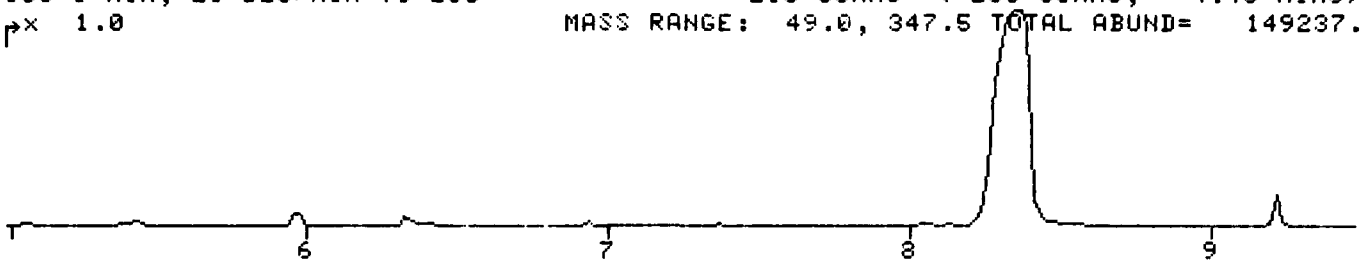
fragments in EI mode to give the two highest mass ions observed, m/z 191 and 175. Further "unzipping" of the ethylene oxide units by successive losses of CH_2O moieties (m/z 30) gives the observed peaks at m/z 161, 145, and 131. The peak at m/z 87 is due to the butoxymethylene ion $C_4H_9OCH_2$. In the earlier described 100°C CI mass spectrum, the presence of a smaller peak at m/z 235 (M-1), in addition to that at m/z 237, constitutes additional evidence in support of the central acetal carbon.

The correctness of this deduced structure was completely confirmed by 1H NMR measurements, recommended by us and performed at Chemical Systems

Laboratory. Data were as follows: 0.8 (triplet, 6H, butyl $\underline{CH_3}$'s), 1.2-1.5 (multiplet, 8H, butyl $\underline{CH_2}$'s), 3.2-3.6 (multiplet, 20 H, $O\underline{CH_2}$'s), and 4.6 (singlet, 2H, $-O\underline{CH_2}O-$).

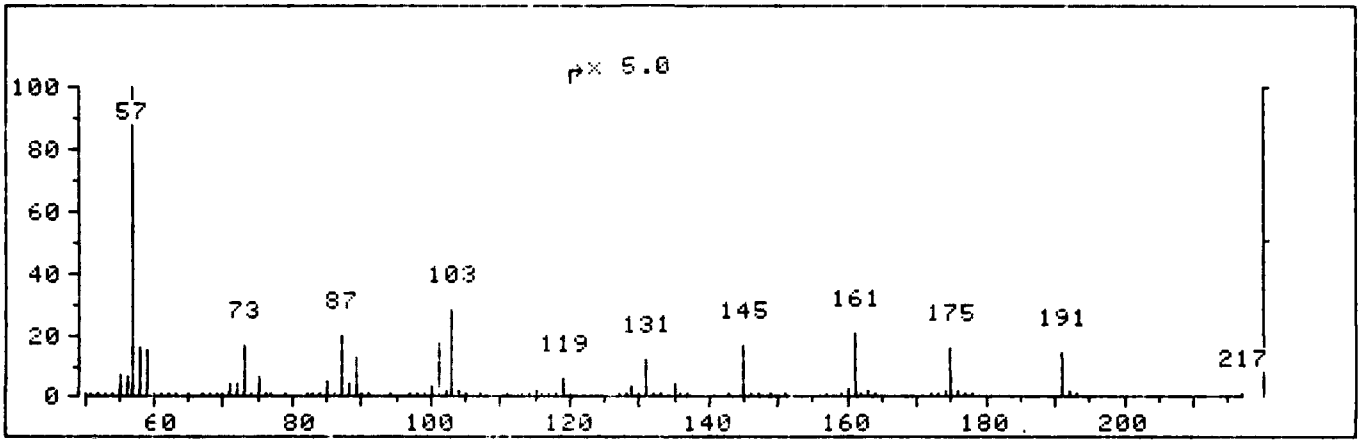
Thus, the identity of the xenobiotic contaminant of the Fort Irwin field water storage and distribution system has been conclusively established as 5,8,11,13,16,19-hexaoxatricosane (common names: butylcarbitol formal and Cryoflex). The compound is used principally as a plasticizer and as a constituent of hydraulic fluids and solid propellants. Its reported toxicity of 1,746 mg/kg (oral LD_{50} in rats)[4] places the compound in the "moderately toxic" category.

FORT IRWIN A3663 FRN 6009, CRN 4
100 1 MIN, 20 DEG/MIN TO 250 206 SCANS (206 SCANS, 4.48 MINS)
↱× 1.0 MASS RANGE: 49.0, 347.5 TOTAL ABUND= 149237.



MINS

155 RET. TIME: 8.37 TOT ABUND= 17109. BASE PK/ABUND: 57.1/ 5326.



FRN 6009, SPECTRUM # 155 RET.TIME: 8.37, 96 PEAKS

M/Z	REL ABUND	M/Z	REL ABUND	M/Z	REL ABUND	M/Z	REL ABUND
51	.7	72	4.0	90	.7	129	.7
53	1.3	73	17.0	98	.5	131	2.4
55	7.5	74	1.0	100	3.3	135	.9
56	6.4	75	6.4	101	17.5	145	3.3
57	100.0	76	.6	102	1.9	160	.5
58	15.8	83	1.5	103	28.5	161	4.1
59	15.4	85	5.0	104	1.8	175	3.2
60	.8	86	1.3	115	1.9	191	2.8
61	.5	87	19.6	117	1.2		
69	1.4	88	4.5	118	1.0		
71	4.6	89	13.1	119	5.8		

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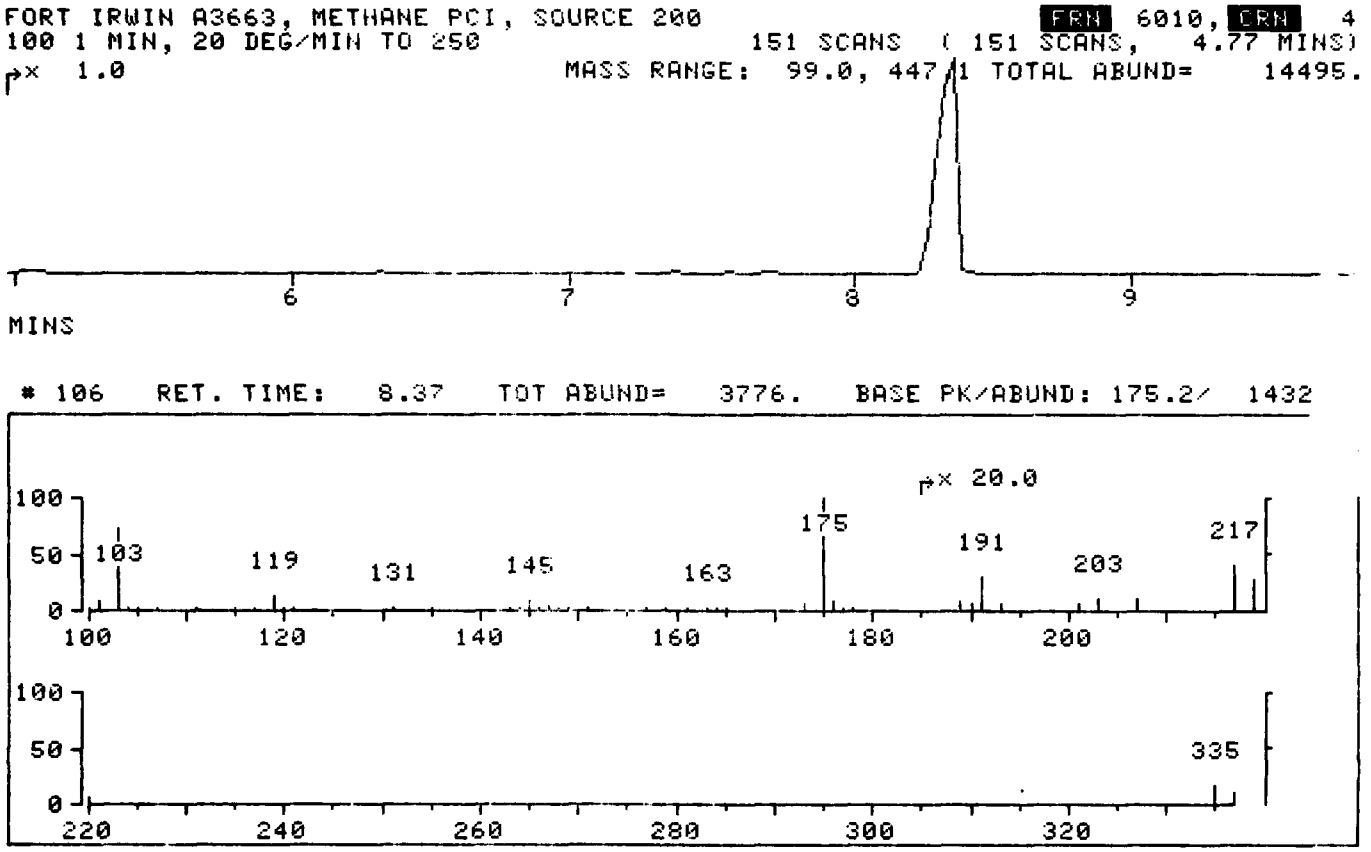
Figure 1. Electron impact mass spectrum of field water supply system contaminant.



FRN 6010, SPECTRUM # 106 RET.TIME: 8.37, 45 PEAKS

M/Z	REL ABUND	M/Z	REL ABUND	M/Z	REL ABUND	M/Z	REL ABUND
100	.8	117	.8	157	.6	189	.5
101	10.1	119	13.3	159	2.1	191	1.5
103	74.2	120	.8	161	1.8	203	.6
104	3.8	131	.9	163	3.8	207	.6
105	1.0	144	.9	173	7.1	217	2.0
107	2.4	145	8.7	175	100.0	219	1.5
111	.6	146	.9	176	10.0	335	.9
115	.8	147	4.5	177	1.0	337	.6

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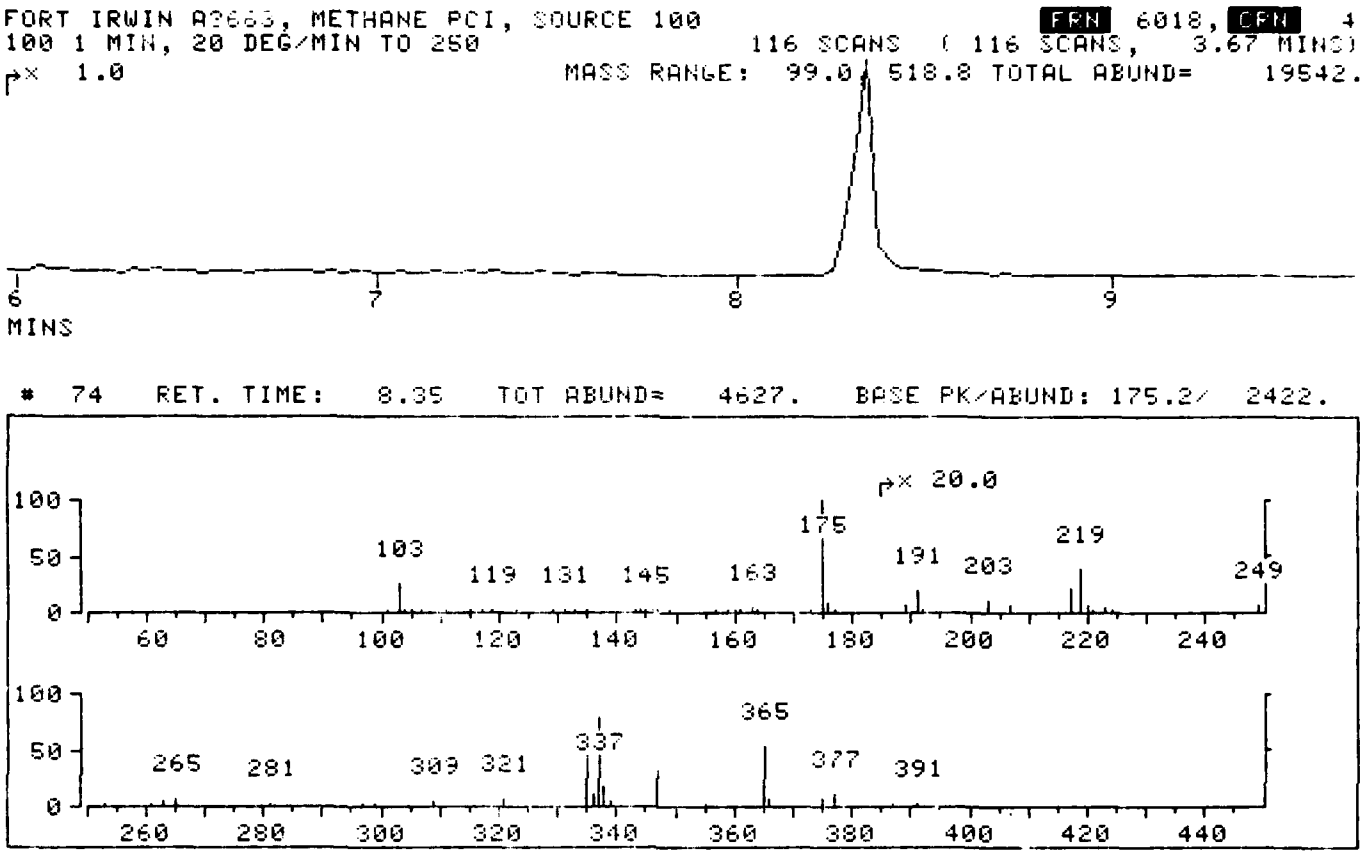
Figure 2. Chemical ionization mass spectrum of field water supply system contaminant, source temperature 200°C.



FRN 6018, SPECTRUM # 74 RET.TIME: 8.35, 65 PEAKS

M/Z	REL ABUND	M/Z	REL ABUND	M/Z	REL ABUND	M/Z	REL ABUND
101	3.5	147	2.0	177	1.5	337	4.0
103	26.2	159	.7	191	1.0	338	.9
104	1.4	161	.9	203	.6	347	1.6
107	1.5	163	6.0	217	1.1	365	2.7
119	3.1	173	2.9	219	2.0	377	.6
143	1.0	175	100.0	335	2.3		
145	2.5	176	10.0	336	.5		

>PAUSE

Figure 3. Chemical ionization mass spectrum of field water supply system contaminant, source temperature 100°C.

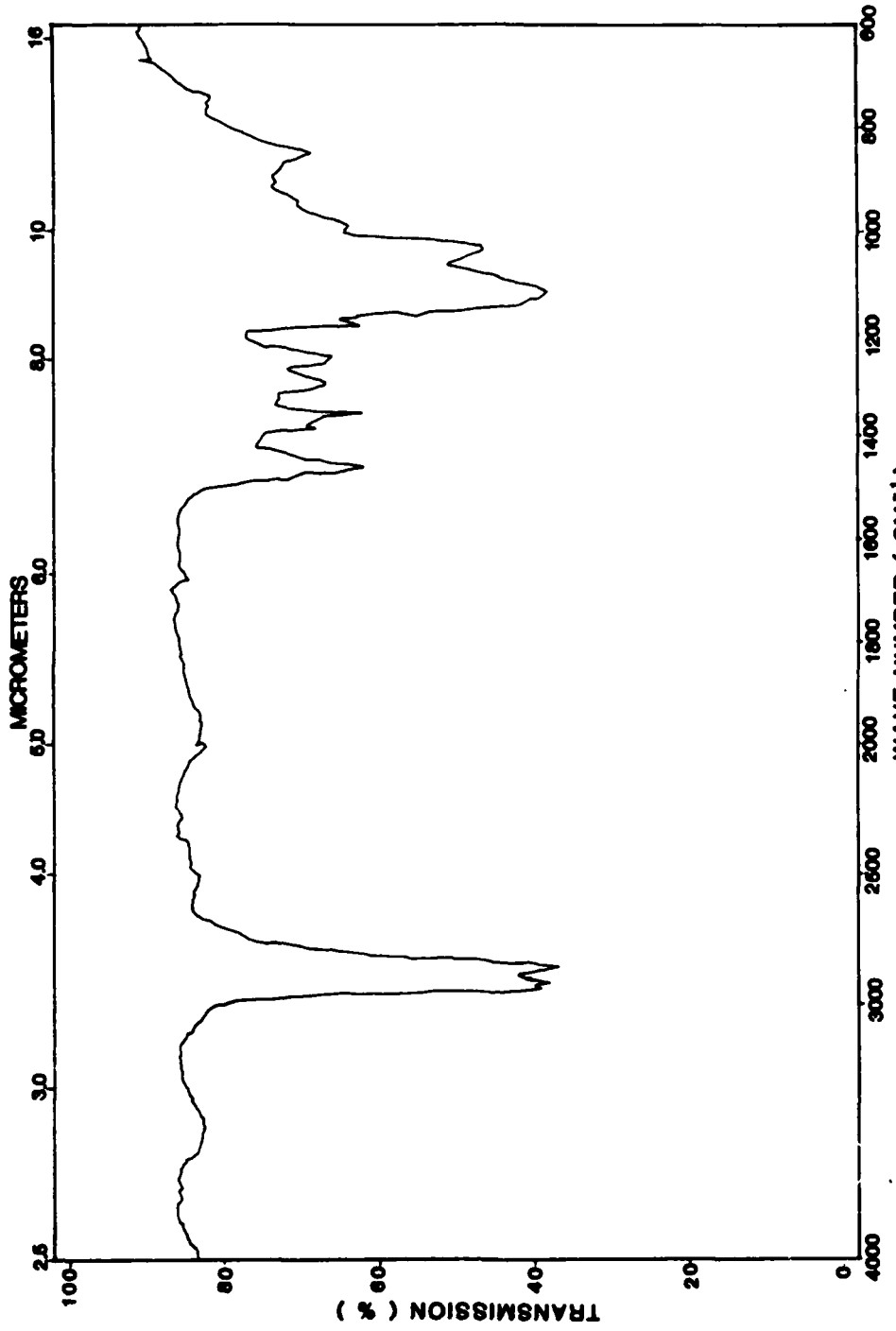


Figure 4. Infrared spectrum of field water supply system contaminant.

REFERENCES

1. Personal communication, LTC Gerald Delaney, Consultant Division, Office of the Army Surgeon General (DASG-PSP), Washington, DC.

2. Personal communication, LTC Niels Biamon, Chief, Water Resources Management Team, Office of The Army Deputy Chief of Staff for Logistics, (DALO-TSE-W), Washington, DC.

3. Millard, B.J. 1979. Quantitative Mass Spectrometry, pp. 5-7. Heyden and Son, Inc., Philadelphia, PA.

4. Lewis, R.J., Sr. and R.L. Tatken, eds. 1980. Registry of Toxic Effects of Chemical Substances, Vol. 2, p. 56. DHHS (NIOSH) Publication No. 81-116. US Government Printing Office, Washington, DC.

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